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IGM88TC-108-779-G
CNRC 29707

DYNAMIC MECHANICAL AND CAPILLARY FLOW BEHAVIOR OF LLDPE/PC BLENDS

by

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To be presented at "ANTEC '89", May 1-4, 1989,

New York, USA

INTRODUCTION

By definition, rheology is a science of interdependence between stress and deformation. Generally, the rheology of miscible polymer blends is easy to measure and relatively simple to interpret. The immiscible systems pose more problems. Here, deformation changes the morphology which in turn modifies the rheological response; the larger the deformation, the larger the morphological change and the more serious the effect on rheology. The evaluation of fundamental properties of immiscible systems is therefore of great interest.

The flow of bis-phenol-A-polycarbonate, PC, and linear low density polyethylene, LLDPE, blend was investigated within the international cooperation research program part of the VAMAS Technical Working Party on Polymer Blends. On the basis of the test results, their repeatability and reproducibility conclusions regarding suitability of the procedure for drawing a standard test method can be assessed. Two types of melt flow were studied: (i) steady state (capillary) and (ii) dynamic mechanical shearing.

EXPERIMENTAL

The characteristics of the homopolymers are listed in Table 1. The granulated resins were dry-blended in a Patterson mixer, then dried in an industrial dryer (Walton-Stout WSD-255) at 100°C for 17 hours. The dried blends were vacuum-fed to a simple screw extruder (Flag-Dawson 25D30V) equipped with a barrier screw (D=6.35 cm, L/D = 30, compression ratio 2.3). The extrusion was carried out at 60 RPM and temperatures (from the feed zone): 217, 230, 231, 237, 249 and 255°C (die). The extrudate passed through chilled rolls (10°C) to a granulator. The granulated blends were re-extruded on commercial line into 2 and 6 mm thick sheets. For rheological measurements, the samples were cut out from the 2 mm sheets. Five blends containing 0, 25, 50, 75 and 100 wt% of PC were prepared.

Prior to the rheological measurements, the specimens were dried for at least 16 hours at 100°C under dynamic vacuum. The steady-state flow properties at 245°C were measured using an Instron Capillary Rheometer, ICR, model 3211. Five capillaries were used at crosshead speed V_x = 0.6, 1.0, 2.0, 6.0, 20 and 60 mm/min. For all measurements, the instrument was filled with a continuous flow of dry nitrogen to prevent an oxidative degradation. Each test was repeated four times and an average value of the force was calculated, F(kg) ± 5%.

The dynamic flow behavior of the blends was carried out using the Rheometrics Mechanical Spectrometer, RMS-605, also at 245°C with either 25 or 50 mm diameter parallel plates. All measurements were performed under a blanket of dry

nitrogen. The rheological response of each blend was measured as a function of strain, time and frequency. Preliminary results of the dynamic testing were previously reported [1]. A comparison between these and capillary flow data will be presented in this paper.

CALCULATION

In capillary flow, the shear rate is not uniform throughout the capillary and the flow pattern changes with capillary radius. In addition, the pressure profile in the die entry region is different from that in the rest of the capillary. To obtain reasonable accuracy of data, the following corrective procedures were incorporated into the computation: a) the shear heating effect; b) the pressure gradient and the entrance-exit effects; c) the Rabinowitsch correction.

a) The shear heating increases the melt temperature in the capillary flow by ΔT above the set barrel temperature, T_b. For the constant rate of shearing, the experimental values of the force can be corrected assuming a simple activated flow:

$$F_{corr} = \phi\bar{F}; \quad \phi = \exp\{nE_\sigma/RT_b[1+T_b/\Delta T]\}; \quad \Delta T = kP/\rho C_p \qquad (1)$$

where F is an average observed load and ϕ is the shear heating correction factor, R is the gas constant, n - power law exponent, k - adiabacity factor (assumed = $\frac{1}{2}$), ρ = density, C_p - specific heat, P - pressure (load), and E_σ - the activation energy of flow at constant stress, σ.

b) The pressure gradient effect and Bagley corrections. Fig. 1 shows a plot of $F_{corr} \propto P$ vs. capillary length-to-diameter ratio L/d. The observed non-linearity has been explained in the literature by the pressure effect on shear viscosity. Recently Utracki [2] reported that η_0 can be expressed as a function of the free volume fraction, $f = f(P,T)$, computed for a given system from the statistical thermodynamic equation of state [3]. A linear correlation was found:

$$\log_{10} \eta_0 = a_0 + a_1/(f+a_2) \qquad (2)$$

where a_i's are parameters.

The main goal of the computation is to correct the Bagley plot in order to extract the true values of shear stress and the entrance-exit correction. To do that, parameters a_i have to be determined. Of these the P-and-T gradient of η_0, the a_1, is the most interesting. It was observed that a_1 depends on the polydispersity index M_w/M_n as well as on

the presence of the incipient phase separation in polymer blends [4].

c) The power-law fluid (Rabinowitsch) correction was calculated using the standard procedure:

$$\dot{\gamma} = \dot{\gamma}_a(3n+1)/4n \qquad (3)$$

where $\dot{\gamma}_a$ and $\dot{\gamma}$ are respectively the apparent and corrected rate of shear at the capillary wall.

DISCUSSION

During the capillary measurements every experimental step was carefully controlled. Nevertheless, as shown in Fig. 2, there is a large scatter of data points reflecting the difficulties encountered in measuring the flow properties of these blends. The large error is associated with the multiphase nature of the incompatibilized LLDPE/PC blends.

The flow of antagonistically immiscible polymer blends was studied by Lin [5]. The author postulated a telescopic flow through a pipe with the interlayer slip:

$$1/\eta = [1+(\beta/\sigma_{12})w_1w_2][w_1/\eta_1+w_2/\eta_2] \qquad (4)$$

where w_i is the weight fraction of component i, σ_{12} is the shear stress and β is the characteristic slip factor. The telescopic flow model predicts a maximum in the log η vs. log σ_{12} curves. As shown in Fig. 3, despite experimental difficulties the agreement between prediction of Eq (4) and the observed dependence is satisfactory; the maximum is indeed experimentally observed. It should be noted that (see Fig. 2) at low deformation rates (or stresses) PC is less viscous than LLDPE, whereas at high rates the reverse is true. For this reason one should expect [6, 7] that at low stresses it is the PC which migrates to the capillary wall, controlling the blend flow behavior, whereas at high stresses it is the LLDPE.

This theoretical prediction is verified experimentally; in Fig. 4 the four Scanning Electron Micrographs are presented. Micrographs a and b show the blend structure after extrusion at $\dot{\gamma} = 6.41(s^{-1})$, or $\sigma_{12} = 24$ kPa, whereas c and d represent the same blend extruded at $\dot{\gamma} = 405\ (s^{-1})$, or $\sigma_{12} = 270$ kPa. Figs. 4a and 4c present the morphology at the center of the freeze-fractured strands, whereas 4b and 4d are taken at the rim. Expecting the thin skin layer in all cases a fibrillar morphology was observed; in 4b the skin is made of PC whereas in 4d it is LLDPE.

The data in Fig. 3 provide an example of the correlation

between the steady state, η, dynamic, η', and complex, η^*, viscosity. For the neat resins $\eta(\sigma_{12}) \simeq \eta'(G'')$ was systematically observed. For the blends such agreement should not be expected. To start with, the morphology in specimens prepared for the dynamic testing is dispersed, and at the low strain of these experiments it remains relatively stable in the full range of frequency [1]. By contrast, as shown in Fig. 4, the morphology of the extrudate is fibrillar, strongly strain dependent. Any agreement between the low strain dynamic viscosity and that measured at high strain in steady state shear would be accidental. As the data in Fig. 3 indicate: $\eta^* \geq \eta' > \eta$. There is up to 40% difference between η' and η.

CONCLUSIONS

1. The dynamic flow measurements are simple to perform, reproducible and reliable for characterization of melt behavior at low strains. The error of the measurements ± 3% was observed. Here the morphology of a multiphase system is relatively stable, unaffected by the test procedure.

2. The large strain capillary rheometry is simple but laborious to perform. In addition, the corrective procedure for extracting the true rheological parameters is complex and lengthy. [For example to characterize the five blends in dynamic test took two days whereas that in capillary flow (several runs for each of the five capillaries) took three months!]. In spite of the utmost care taken during these measurements, extensive repeatability and corrective computations, the error of measurements was ±30%, reflecting the highly variable nature of blend morphology in the large strain steady state flow.

3. For characterization of multiphase materials the low strain dynamic test should be used. For systems with strain-dependent morphology the capillary flow tests should be avoided at all cost.

ACKNOWLEDGEMENT

The morphological analysis of these blends was performed by Dr. B.D. Favis of this Institute.

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Table 1. CHARACTERISTIC PARAMETERS OF PC AND LLDPE

No.	Property	PC	LLDPE[a]
1.	Manufacturer	General Electric Co.	Esso Chemicals Canada
2.	Type/grade	Lexan RL 5230-111N /Injection	Escorene/extrusion
3.	Lot	LK 0208T	LL 1030.28
4.	Melt Index (g/10 min)	9.5	0.5
5.	Density (kg/m^3)	1200	918
6.	Molecular Weight[b] (kg/mol)		
	M_n		44 ± 13
	M_z		342 ± 19
	M_w/M_n		3.8 ± 0.6

Notes: (a) Random copolymer with 15.8 mol% of butene; Run No. 0.03378 [7].

(b) From size exclusion chromatography in polystyrene-equivalents.

LEGEND FOR FIGURES

Fig. 1 Bagley plot of the corrected load, F_{corr}, vs. the capillary length-to-diameter ratio, L/d, at crosshead speed V_x = 0.6 to 60 mm/min.

Fig. 2 Summary of the capillary flow results for homopolymers and two blends containing 25 and 50 wt% PC at 245°C. The corrected viscosity, η, is plotted vs. shear stress, σ_{12}. The bars at 45° indicate the experimental uncertainty of the measurements.

Fig. 3 Comparison between the steady state viscosity, η, and low strain dynamic, η', and complex, η^*, viscosity of 50 PC blend. The solid line was computed from Eq (4). The 45° bars indicate experimental error in capillary measurements. Note presence of an apparent yield stress in the low frequency dynamic data.

Fig. 4 The scanning electron micrographs of 25 wt% PC blend after capillary extrusion at σ_{12} = 24 (a and b) or 270 (c and d) kPa; extrudate center (a and c), edge (b and d).

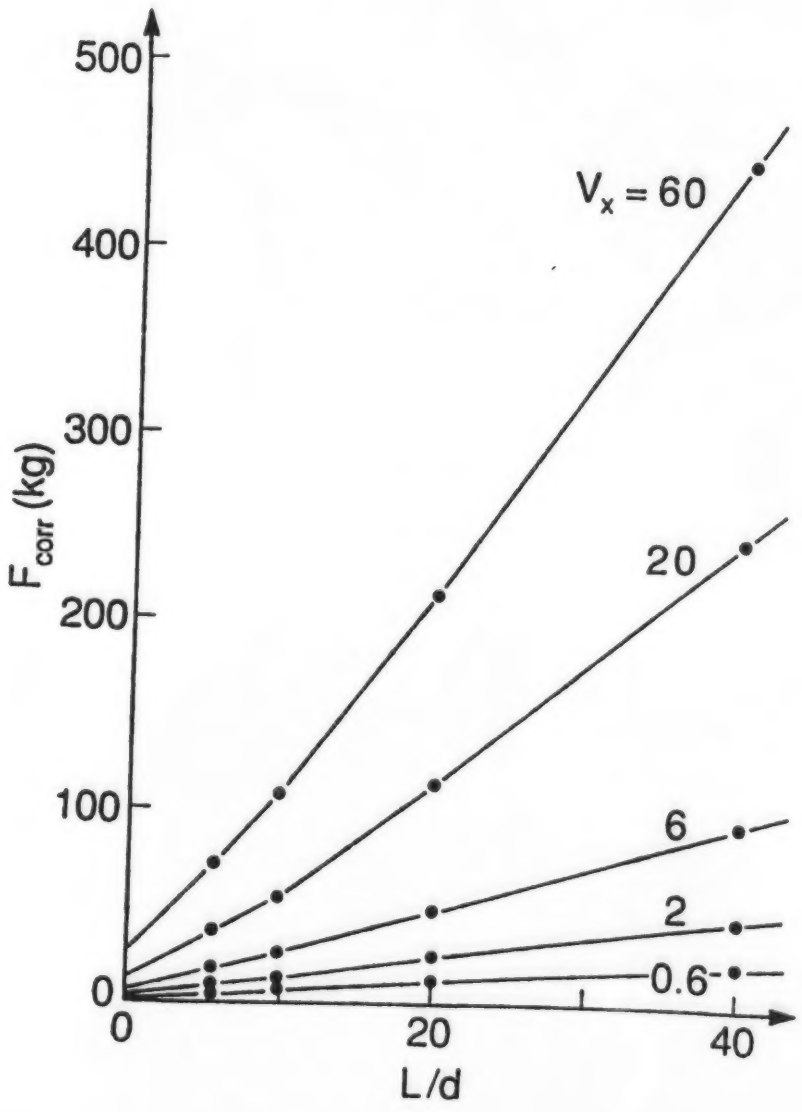


Fig. 1 Bagley plot of the corrected load, F_{corr}, vs. the capillary length-to-diameter ratio, L/d, at crosshead speed V_x = 0.6 to 60 mm/min.

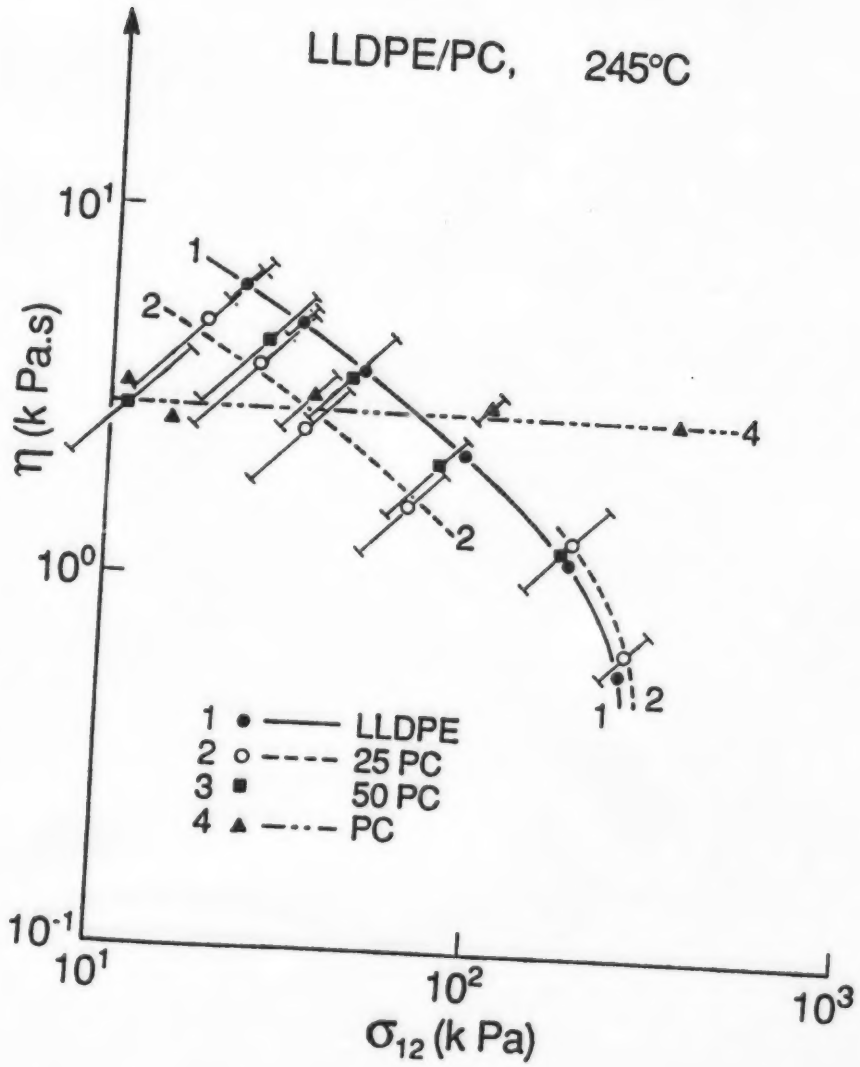
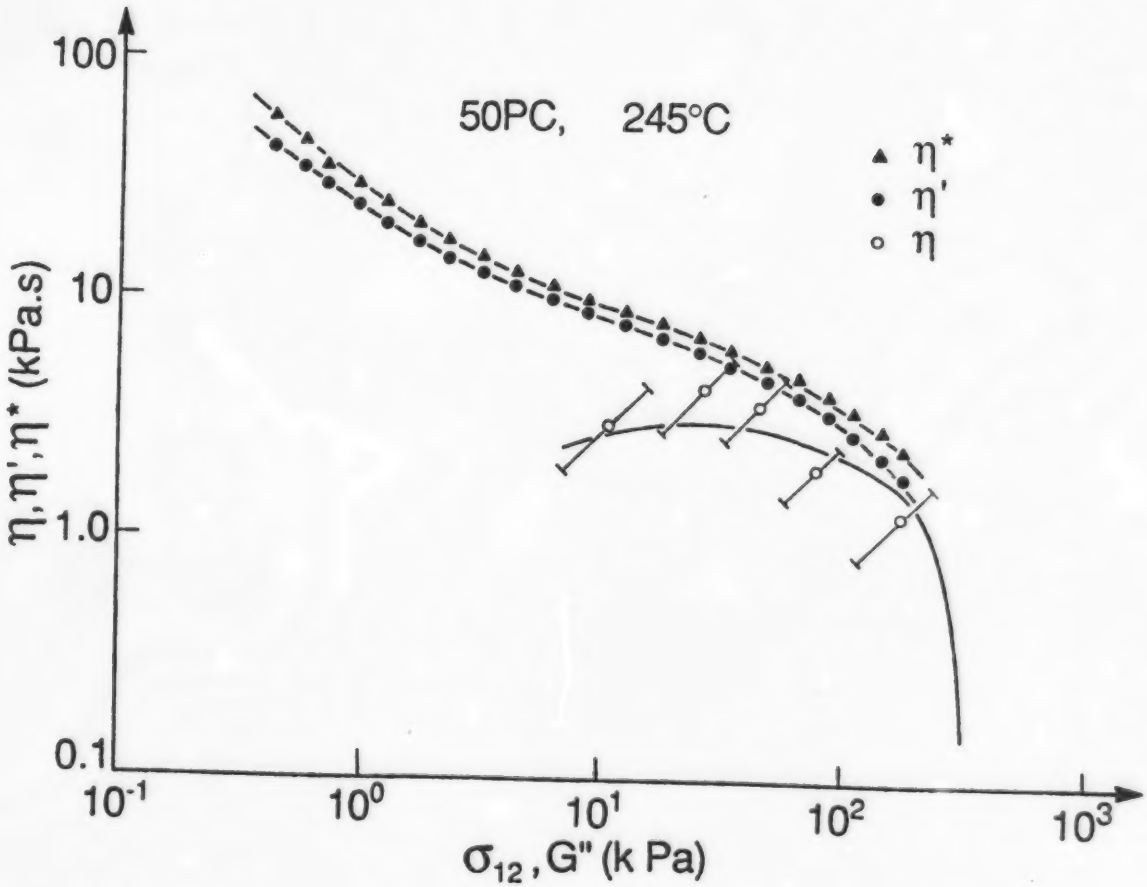


Fig. 2 Summary of the capillary flow results for homopolymers and two blends containing 25 and 50 wt% PC at 245°C. The corrected viscosity, η, is plotted vs. shear stress, σ_{12}. The bars at 45° indicate the experimental uncertainty of the measurements.



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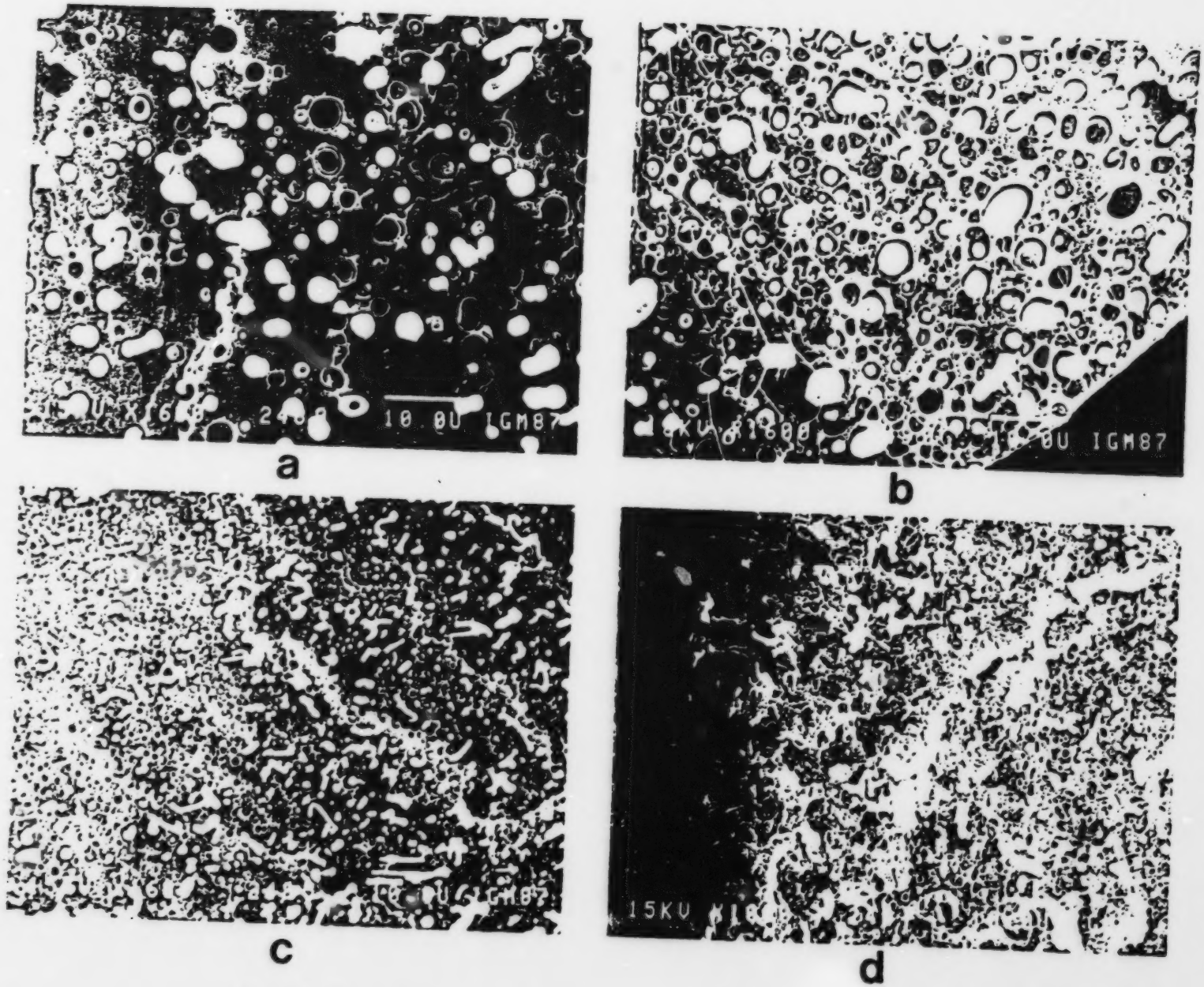

Fig. 4 The scanning electron micrographs of 25 wt% PC blend after capillary extrusion at $\dot{\gamma}_w$ = 24 (a and b) ...

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